



Alkoxy substituted imidazolium-based ionic liquids as electrolytes for lithium batteries

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HIGHLIGHTS

- Novel alkoxy-imidazolium ionic Liquids as electrolytes for lithium batteries.
- Safer mixtures based on alkoxy-IMITFSI and organic carbonates.
- R.t. conductivity $>5 \text{ mS cm}^{-1}$ in case of IMITFSI with the shorter ether side chain.

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ABSTRACT

The design and the optimization of new electrochemically stable and safer electrolytes for both Li-ion and Li-air/Li-O₂ batteries is a key-target in the field of clean energy. Ionic liquids (ILs) were often indicated as components of the electrolytes of the future, because they could fulfil all the requirements for the use in electronic devices and they also address the safety issues for large-scale applications.

In this work, two ether-functionalized ILs, namely 1-(2-methoxyethyl)-3-methylimidazolium TFSI (IMI_{1,201}TFSI) and 3-(2-(2-methoxyethoxy)ethyl)-1-methylimidazolium TFSI (IMI_{1,10201}TFSI) were synthesized and characterised from a physical and electrochemical point of view. The thermal features, viscosity, conductivity and electrochemical stability were compared with those of an alkyl-IMITFSI (BuMeIMITFSI) in order to evaluate the influence of the alkoxy-groups on the electrolyte performances. Preliminary battery tests in Li/LiFePO₄ cells containing solutions of IL-LiTFSI mixed with EC/DEC as electrolytes were also performed to address the cycling behaviour and the delivered capacity.

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1. Introduction

It is well known that ionic liquids (ILs) are key-materials for the future design of safer electrolytes for lithium batteries [1,2]. Their unique properties, in terms of non-flammability and hydrophobicity, as well as good ionic conductivity and electrochemical performances, make them potential targets also for applications in Li/air or Li/O₂ cells [3–5]. However, some important questions are still open, namely electrochemical instability above 4 V and reactivity towards lithium. Several approaches to overcome these limiting factors were recently proposed in literature, such as the use of new cations and anions (e.g. (FSO₂)₂N[−]), the preparation of mixtures with conventional organic carbonates, the preparation of gel and/or composite electrolytes [1,2,6–9]. Among the wide spectrum of proposed structures (see for instance ref. [6]), 1-methyl-4-butyl-

pyrrolidinium-bis(trifluoromethanesulfonylimide) (PYR_{1,4}-TFSI) is considered a very promising electrolyte for Li batteries due to its hydrophobicity, wide electrochemical window, and high ionic conductivity in the molten phase. However, it easily crystallizes below 0 °C and this obviously may cause dramatic conductivity drops in the temperature working range of the battery. Moreover, its viscosity is still too high, if compared to that of standard organic electrolytes. In order to explore other potential ILs as liquid electrolytes, our groups recently proposed novel methylpyrrolidinium-based structures (PYR_{1,OR}-TFSI), derivatized with ethoxy-containing side chains [10–12]. Two systems were proposed, namely PYR_{1,201}-TFSI and PYR_{1,20201}-TFSI, with substituents differing for the chain length and the number of the oxygen units. We observed that the presence of ether-groups hinders the crystallization below room temperature, likely due to interactions between the oxygen atoms of the functionalising group and the large neighbouring imide anion. Amorphous systems were, in fact, obtained in both cases, with glass transition temperatures, *T*_g, below −80 °C, depending on the side chain length [10,11]. These features were also observed in

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other cyclic quaternary ammonium salts, as, for instance, pyrazolinium-, piperidinium, morpholinium, oxazolidinium-based ones [13,14]. In addition, the oxygen units were proved to decrease the IL viscosity. Values of $\eta_{20^\circ\text{C}}$ of the order of 40 cP were obtained in case of $\text{PYR}_{1,201}$ -TFSI, with consequent promising enhancements of the ionic conductivity (2.9 mS cm^{-1} at 20°C) [10,12].

The idea to introduce ether chains as lateral substituents in the ionic liquids also leads from what observed for the poly(ethylene-oxide)-based electrolytes. Similarly to what found in case of PEO-LiX systems, even in the Li-doped alkoxy-ILs, the ether oxygen, for instance, might activate strong physical and chemical interactions with the Li^+ cations, causing interesting effects on the carrier migration mechanism and conductivity.

Other beneficial effects related to the addition of the ether-groups in PYR-TFSI systems are the inhibition of self-aggregation phenomena between cation and neighbouring anions [15], as well as the improvement of polarity and salt solubility [16,17]. Contrary to alkyl-PYR systems, solutions of $\text{PYR}_{1,201}$ -LiTFSI with a wide salt concentration range (up to 0.7 m) were also prepared without drops in conductivity with respect to the pure IL [10].

In order to evaluate the actual efficiency of the oxygen-based functionalization in the optimization of the ionic liquids as energy storage materials, it is interesting to investigate this cation modification also in Imidazolium (IMI)-based systems. IMI-based ionic liquids were fully characterised and tested as electrolytes in lithium batteries [1,6] because of the easy synthesis, lower viscosity and higher ionic conductivity with respect to the pyrrolidinium family. However, they also show a poor cathodic stability related to reduction processes obtained in consequence of the imidazolium electrochemical deprotonation around 1.5 V. This feature limits their use in combination with low-voltage anodes such as lithium metal, graphite, Li titanates [18]. Some attempts to prepare alkoxy-based imidazolium ionic liquids as electrolytes for rechargeable Li batteries were recently reported in the literature. Aurbach, for instance, synthesized and tested 1-(2-methoxyethyl)-3-methylimidazolium-TFSI (MEMI-TSFI) as electrolyte for 5 V cell with Li metal anode and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode [19]. However, to our knowledge, poor information is still available in the literature about the relationships between the structure of imidazolium-based systems with alkoxy-side chains and their physical, chemical and electrochemical properties.

In this paper, we studied two ether-derivatized imidazolium ionic liquids as electrolytes for rechargeable Li batteries, with two different cations, namely 1-(2-methoxyethyl)-3-methylimidazolium and 3-(2-(2-methoxyethoxy)ethyl)-1-methylimidazolium (labelled in the following as $\text{IMI}_{1,201}$ and $\text{IMI}_{1,10201}$, respectively), but the same anion, bis(trifluoromethanesulfonyl)imide (TFSI). The cations differ for the number of oxygens and the length of the side chain. The physical properties and the electrochemical performances of both pure ILs and their solutions with LiTFSI as Li ions sources are described and discussed in terms of the different cation structure. The system based on 1-butyl-3-methylimidazolium ($\text{IMI}_{1,4}$) is also examined for the sake of comparison. In order to evaluate the eventual beneficial effects of the standard organic carbonates on the ionic liquids electrochemical performances, different mixtures of $\text{IMI}_{1,201}$ and $\text{IMI}_{1,10201}$ and EC/DEC binary systems were also produced by varying

the LiTFSI concentration. The conductivity, viscosity, thermal features, electrochemical window and cycling behaviour in a LiFePO_4 -based cell were also investigated.

2. Experimental

2.1. Synthesis of imidazolium- $\text{N}(\text{SO}_2\text{CF}_3)_2$ (IMI-TFSI) ionic liquids

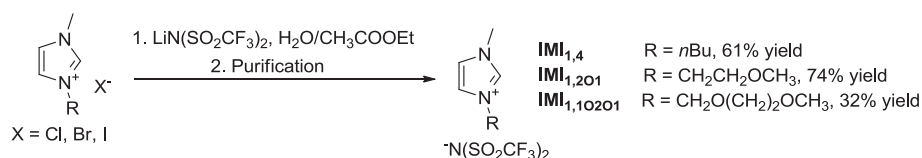
Three different imidazolium-TFSI ionic liquids, labelled in the following as $\text{IMI}_{1,4}$, $\text{IMI}_{1,201}$, $\text{IMI}_{1,10201}$ were prepared by means of the synthetic approach described in Scheme 1 [20–22]. In detail, a solution of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) in water was added to a mixture of the proper organic halide in ethyl acetate ($\text{IMI}_{1,4}$: 1-butyl-3-methylimidazolium bromide; $\text{IMI}_{1,201}$: 1-(2-methoxyethyl)-3-methylimidazolium bromide; $\text{IMI}_{1,2(02)01}$: 3-(2-(2-methoxyethoxy)ethyl)-1-methylimidazolium chloride). The resulting biphasic system was stirred at room temperature for 24 h. The organic layer was separated, washed with water and the solvent evaporated in vacuum. Purification of the crude IL involved treatment with activated charcoal (to remove organic impurities), extraction with water in a liquid–liquid continuous extractor (to eliminate inorganic contaminants) and a drying process with activated alumina. The elemental analysis and spectroscopic characterization of the pure ILs (not reported here) are in fair agreement with what reported in the literature [21–23]. The water content of all the ionic liquids was less than 30 ppm, as detected by means of Karl–Fisher technique.

2.2. Preparation of LiTFSI-(IMI-EC-DEC) liquid electrolytes

LiTFSI-doped solutions of $\text{IMI}_{1,201}$ and $\text{IMI}_{1,10201}$ with EC/DEC binary system (1/1 v/v) were prepared in dry box (H_2O , $\text{O}_2 < 1 \text{ ppm}$) under argon atmosphere by dissolving proper salt amounts in the mixture of solvents so to obtain concentrations of 0.5 M and 1.0 M. The volume ratio between the ionic liquid and the mixture EC/DEC was 60/40 v/v.

2.3. LiFePO_4 cathode preparation and cell assembly

The LiFePO_4/C cathode material was obtained by hydrothermal synthesis in presence of an organic surfactant, as reported in our previous work [24]. The LiFePO_4/C composite electrode was prepared by spreading a slurry of the active material on an Al current collector by means of a doctor blade. The slurry was composed by LiFePO_4 (70 wt%, typically $\sim 3 \text{ mg cm}^{-2}$), acetylene black (20 wt%) and poly(vinylidene fluoride) (10 wt%, PVdF, Solvay Solef 6020), dispersed in N-methyl-2-pyrrolidone (NMP, Aldrich). After evaporation of the solvent, disks of 0.785 cm^2 were punched out of the foil and dried by heating overnight at 100°C . The lithium cells were assembled by contacting in sequence a lithium metal (Aldrich) disk anode, a separator imbibed with the liquid electrolyte and a disk of the composite cathode. The electrodes/electrolyte assembly was housed in a Teflon-made Swagelok cell (area 0.785 cm^2), equipped with two stainless-steel SS-316 current collectors. Both electrode fabrication and cell assembly were performed in an environmentally controlled Ar-filled dry box.



Scheme 1. Synthetic procedure of IMIsTFSI ionic liquids.

2.4. Characterizations

NMR spectra of $\text{PYR}_{1,0\text{R}}$ were recorded on a 300 MHz spectrometer (Bruker). The attributions of the signals of the ^1H and ^{13}C NMR spectra were supported by DEPT-135 experiments. The DSC measurements were performed with a 2910 MDSC (TA Instruments) by using aluminium pans, at a rate of 5°C min^{-1} under nitrogen purge. TGA scans were recorded at 5°C min^{-1} under nitrogen flow with a 2950 TGA (TA Instruments). The viscosity was measured at $20 \pm 1^\circ\text{C}$ by means of a rotational viscosimeter (Rheotec, mod. RC20) with a cone-plate configuration, in control shear rate mode. The ionic conductivity was measured by means of the impedance spectroscopy technique, using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 1 Hz–1 MHz, by applying a voltage of 100 mV. The impedance scans were carried out in the temperature range between -28°C and 80°C , by using a two-probes liquid cell with Pt electrodes and cell constant of 0.3 cm^{-1} . In order to study the electrolyte stability vs Li, potentiodynamic sweeps were performed by means of an Electrochemical Interface Solartron 1287 on a three electrodes cell using lithium as both the counter and the reference electrodes and nickel as the working one. A Whatman glass microfiber filter was used as separator. In the case of pure IMI ionic liquids, the three-electrode cell (Cypress Systems) was made of glassy carbon as the working electrode, a Pt wire as the counter one and Ag/Ag^+ (CH_3CN , 1 mM AgNO_3) as the reference. The effective electrode area of the glassy carbon electrode, 0.033 cm^2 , was calculated from cyclic voltammograms on a 1 mM ferrocene solution in CH_3CN (0.1 M tetrabutylammonium perchlorate), by applying the Randles-Sevcik equation to the resulting peak current:

$$i_p = 0.4463nF(nF/RT)^{1/2}AD^{1/2}v^{1/2}c \quad (1)$$

where i_p is the peak current, n is the number of electrons in the charge transfer step, A is the electrode area, D is the diffusion coefficient of Fc ($2.5 \cdot 10^{-5}\text{ cm}^2\text{ s}^{-1}$), c is the concentration and the v the scan rate (10 mV s^{-1}). The $\text{Li}/\text{LiFePO}_4$ cells were tested at room temperature in terms of charge/discharge galvanostatic cycling (cut off voltages to 2.50–4.00 V vs Li^+/Li , starting from O.C.V.) at different current regimes using an Arbin Instrument Testing System model BT-2000.

3. Results and discussions

3.1. Thermal properties of pure IMI-TFSI ionic liquids and Li-doped IMI-EC/DEC mixtures

The ILs thermal stability was studied by means of thermogravimetry in the temperature range 25°C – 600°C . Fig. 1a compares the TGA plots of the two alkoxy-imidazolium-TFSI ILs with that one of the alkyl-based system. Both $\text{IMI}_{1,4}$ -TFSI and $\text{IMI}_{1,201}$ -TFSI show one-step decomposition starting at temperature higher than 350°C , similarly to the corresponding alkoxy-PYR systems [10]. Their thermal stability is remarkably higher than that of the alkyl-PYRs, where decompositions onset in the range 189°C – 230°C were observed, depending on the cation structure [25]. The alkoxy-imidazolium salt with the longer lateral chain, $\text{IMI}_{1,10201}$, shows a lower thermal stability. A first minor decomposition with a weight loss of about 20 wt% takes place at $\sim 250^\circ\text{C}$, followed by the main one, which occurs at lower temperatures than those detected in case of the other IMIs. Such differences in the thermal stability may be reasonably ascribed to the different length of the side chain, rather than the number of oxygen units. Similar trends were, for instance, observed for the pyrrolidinium system, where lower

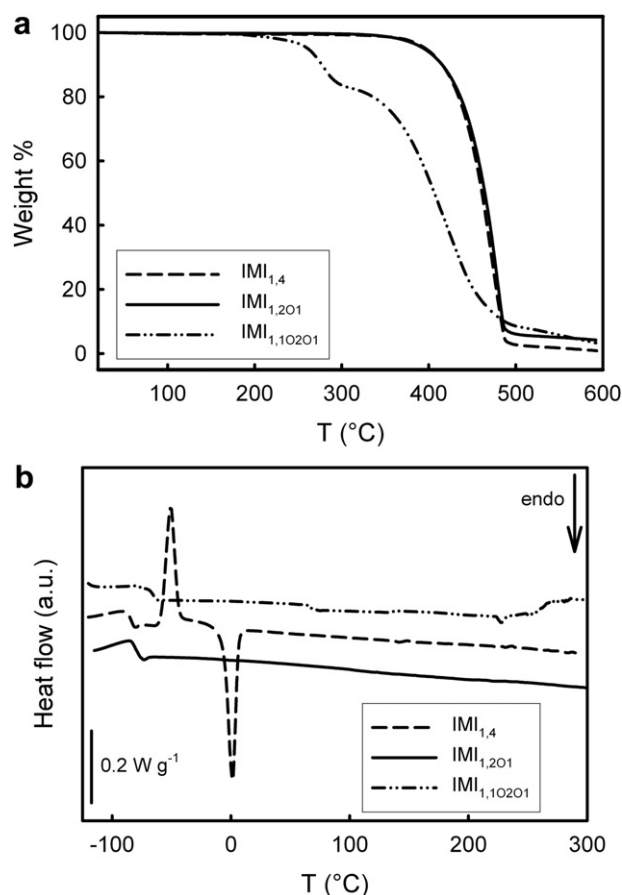


Fig. 1. TGA (Part a) and DSC (Part b) thermograms of the pure IMIs-TFSI ionic liquids.

decomposition onsets were detected in presence of larger substituents [25]. Roughly residual weights of 1–4% of the pristine ionic liquids are found after the decomposition process heating the samples under N_2 atmosphere.

The TGA plots of the EC/DEC-based mixtures (not reported here) show weight losses of about 20% between 70° and 150°C , due to the evaporation of the solvents. This is somehow expected, considering the lower thermal stability of the organic carbonates. The onset of the main decomposition step, however, does not change. Similar results were found for PC/ $\text{PYR}_{1,4}$ TFSI-based electrolytes [8].

Fig. 1b shows the DSC heating traces of the alkoxy-IMIs and $\text{IMI}_{1,4}$. The alkyl-imidazolium IL shows a glass transition at -87°C , in fair agreement with the literature [26] followed by cold crystallization (-60°C) and melting (0°C). In contrast, the alkoxy-IMIs are characterised only by glass transitions and no other thermal features are observed in the battery working range of temperature. As already stated before, the presence of ether-groups in TFSI-based systems seems to hinder crystallization/melting processes. An analogous situation was found in case of ether-functionalized ionic liquids with different cationic structures, such as pyrrolidinium and pyrazolinium [10,13]. These results were interpreted in terms of high flexibility of the ether groups, as well as of decreased lattice energy of the ionic liquid in consequence of a reduced symmetry of both cation and anion. The thermal properties of the ILs are correlated to the ion crystal packing rearrangements which become more significant in presence of ether groups, due to the repulsive interactions between the oxygen electron lone pair of neighbouring –OR units and the anions [27].

Table 1 reports the glass transition temperatures, T_g , of three imidazolium ionic liquids. Similarly to what already observed for PYR-based systems [10], higher values of T_g are measured in presence of alkoxy-substituents. In particular, the glass transition occurs at higher temperature (200 K) in case of IMI with the longer ether-chain, IMI_{1,10201} than those found for IMI₁₂₀₁ (192 K). This could be interpreted, again, in terms of interactions between the oxygen units and the neighbouring anion, which stiffen the system. No significant differences in the thermal features may be observed in case of mixtures based on alkoxy-IMI with EC/DEC and doped with two different LiTFSI concentrations, namely 0.5 and 1.0 M. The glass transition temperatures remain almost unchanged in presence of carbonates and/or high Li ions contents, in agreement with what recently observed for Li salt-doped imidazolium ionic liquids [28].

3.2. Viscosity and ionic conductivity of the pure IMI-TFSI ionic liquids and Li-doped IMI-EC/DEC mixtures

Table 1 compares several physical properties of the pure ionic liquids with those of the Li salt-doped IL/EC/DEC mixtures, namely viscosity, density and ionic conductivity at 20 °C.

As already stated in the experimental part, mixtures with a volume ratio between the ionic liquid and the binary system EC/DEC of 60/40 v/v were considered. The choice of such a composition was suggested by preliminary physical and chemical studies performed on similar solutions, prepared by using PYR_{1,201}TFSI as ionic liquid and the same organic carbonates as co-solvents. In this latter case, in fact, the mixture 60/40 resulted to be the best system in terms of non-flammability, ionic conductivity, room temperature viscosity and overall electrochemical stability.

Except for the high value observed in case of IMI_{1,201} ($d = 1.83 \text{ g cm}^{-3}$), probably related to a stronger tendency of molecular aggregation, the density measured for the pure IMIs ranges between 1.30 g cm^{-3} and 1.49 g cm^{-3} , in fair agreement with what generally determined for the imidazolium ionic liquids [6]. The presence of one or more oxygen in the side chain does not change strongly the viscosity of the pure system, which remains almost constant around 35 cP at 20 °C. However, when the cation is modified with a longer chain, the IMI becomes more viscous and values of viscosity of 67 cP are measured for IMI_{1,10201}. As expected, the addition of large amounts of organic carbonates to the ILs (40 vol%) remarkably decreases the viscosity. The ionic conductivity of ILs clearly reflects the viscosity trend. Fig. 2 compares the conductivity of the pure alkoxy-IMIs and IMI_{1,4in} in the temperature range between -28° and 80°C . Contrary to what noticed for the ether-PYR family [10], the modification of the IMI cation with a short side ether-group does not affect the conductivity. Values exceeding 4.2 mS cm^{-1} are obtained for IMI_{1,201}TFSI, without significant drops in conductivity below room temperature. Conductivity values lower by about a factor of two are, in contrast, found for IMI_{1,10201}TFSI, in agreement with the viscosity data.

Fig. 3 shows the conductivity behaviour between -28° and 80°C for the solutions prepared by mixing the alkoxy-IMIs and EC/DEC at different concentrations of LiTFSI. The IMI_{1,201}TFSI-LiTFSI 1.0 M sample is also reported as a comparison. By the analysis of both table and figure, some considerations may be outlined. First, the conductivity of the mixtures decreases by increasing the Li salt concentration. This aspect is particularly evident in case of the smaller ether-based IMI (IMI_{1,201}TFSI), whose ionic conductivity falls of a factor of two when LiTFSI is added in a 1.0 M concentration ($\sigma_{20^\circ \text{C}} < 1 \text{ mS cm}^{-1}$). However, these drops may be easily balanced by adding proper amounts of organic carbonates; values of 5.80 mS cm^{-1} and 4.33 mS cm^{-1} are, in fact, reached at 20°C in case of the mixture IMI_{1,201}TFSI-EC/DEC-LiTFSI 0.5 M and IMI_{1,10201}TFSI-EC/DEC-LiTFSI 0.5 M, respectively (see Fig. 3 and Table 1). Similar positive effects of the organic carbonates in the transport and electrochemical properties of the Li-doped ionic liquids were recently observed also by other groups [8,9]. Passerini and co-workers, for instance, found enhancements of conductivity up to a factor of 5 by adding 50 wt% of propylene carbonate to the solution PYR_{1,4}TFSI-0.3 M LiTFSI [8].

Both pure IMIs and Li-doped mixtures show conductivity behaviours very well described by the Vogel–Tammann–Fulcher (VTF) equation [29]

$$\sigma(T) = AT^{-0.5}e^{-\frac{B}{T-T_0}} \quad (2)$$

where A is the pre-exponential factor, T_0 is a reference temperature which may be ascribed to an ideal glass transition temperature, usually falling in the range 20–50 K below the T_g , and B is a pseudo-activation energy for the charge-carriers motion. The VTF equation (2) is a phenomenological way to interpret ion transport (or viscosity) data in amorphous polymer electrolytes above the glass transition [30]. In particular, VTF behaviours of viscosity and conductivity have been reported for ionic liquids [31]. The VTF parameters can be obtained by proper linearization of equation (2). The values of the best-fitting parameters B and T_0 for both pure ILs and mixtures are reported in Table 1. A maximum of pseudo-activation energy is observed in case of the alkyl-IMI (IMI_{1,4}, $B = 1026 \text{ K}$). Significantly lower B values are, in contrast, calculated when an alkoxy group replaces an alkyl one in the IMI cation. T_0 values in the range 124–165 K have been determined for the IMIs as well as the mixtures, in good agreement with the calorimetric glass transition temperatures obtained by DSC (see Table 1).

3.3. Electrochemical stability

Fig. 4 reports the linear voltammetry curves of the pure IMI-based ionic liquids, collected at 10 mV s^{-1} . Both the alkyl- and alkoxy-imidazolium liquids show comparable cathodic and anodic limits, and electrochemical stability windows (ESW) wider than 5 V vs Fc/Fc^+ are generally observed. In particular, IMI_{1,201} shows an ESW of 5.3 V, from -2.5 V to 2.8 V vs Fc/Fc^+ . Contrary to what found

Table 1

Physical and electrochemical parameters of the IMIs-based ionic liquids and electrolytes: density, d ; viscosity, η ; conductivity, σ , measured at 20°C ; VTF fitting parameters, B and T_0 , with the fit goodness, r^2 ; cathodic and anodic limits, E_{cath} and E_{an} .

| Electrolyte | $d_{20^\circ \text{C}} (\text{g cm}^{-3})$ | $\eta_{20^\circ \text{C}} (\text{mPa s})$ | $T_g (\text{K})$ | $\sigma_{20^\circ \text{C}} (\text{S cm}^{-1})$ | B | $T_0 (\text{K})$ | r^2 | $E_{\text{cath}} (\text{V})$ | $E_{\text{an}} (\text{V})$ |
|---|--|---|------------------|---|------|------------------|--------|------------------------------|----------------------------|
| IMI _{1,4} | 1.30 | 34.7 | 186 | 4.38 | 1026 | 124 | 0.9997 | 0.8 | 3.9 |
| IMI _{1,201} | 1.83 | 33.5 | 192 | 4.26 | 784 | 148 | 0.9997 | 0.7 | 4.4 |
| IMI _{1,10201} | 1.49 | 67.3 | 200 | 1.88 | 165 | 165 | 0.9999 | 1.0 | 3.6 |
| IMI _{1,201} -EC/DEC LiTFSI 0.5 M | 1.63 | 24.9 | 191 | 5.80 | 704 | 135 | 0.9997 | 1.9 | 3.3 |
| IMI _{1,201} -EC/DEC LiTFSI 1.0 M | 1.75 | 27.7 | 189 | 4.40 | 612 | 160 | 0.9999 | 2.2 | 4.0 |
| IMI _{1,10201} -EC/DEC LiTFSI 0.5 M | 1.54 | 22.5 | 195 | 4.33 | 145 | 145 | 0.9999 | 2.1 | 4.1 |
| IMI _{1,10201} -EC/DEC LiTFSI 1.0 M | 1.59 | 24.0 | 200 | 2.68 | 153 | 153 | 0.9999 | 2.2 | 4.2 |

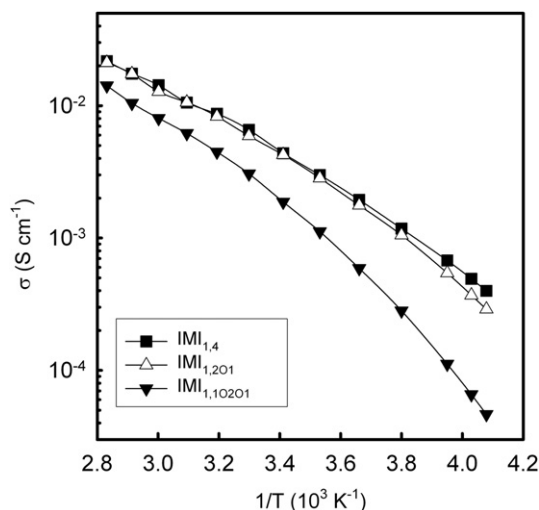


Fig. 2. Ionic conductivity plots as a function of the temperature for the pure IMIs-TFSI ionic liquids. The lines are only guides for eyes.

in literature for other systems, as for instance pyrrolidinium-based ones [11,32], the introduction of a longer chain or alkoxy-groups as lateral substituents does not seem to affect the reduction process of the cation. However, smaller electrochemical phenomena are also observable between 2 and 3 V, in particular for what concerns IMI_{1,4}- and IMI_{1,201}-based systems. Such features may be likely due to the degradation of impurities eventually present in the ionic liquids.

Fig. 5 shows, as an example, the linear voltammetry sweeps vs Li/Li⁺ of the pure alkoxy-IMIs-based ionic liquids, IMI_{1,201}TFSI and IMI_{1,10201}TFSI, and of the mixtures IMI_{1,201}TFSI-EC/DEC-LiTFSI, 0.5 M and 1.0 M respectively. The scans were collected at a scan rate of 0.2 mV s⁻¹. Both cathodic and anodic limits of the other investigated systems, which are due to the cation and anion decomposition, respectively, are reported in Table 1. With regards to the pure IMIsTFSI, no remarkable differences in the electrochemical stability are observed by comparing IMI_{1,4}TFSI and IMI_{1,201}TFSI. In both cases, ESWs of about 4 V are measured. In contrast, the alkoxy-imidazolium system with the longer ether side chain is less

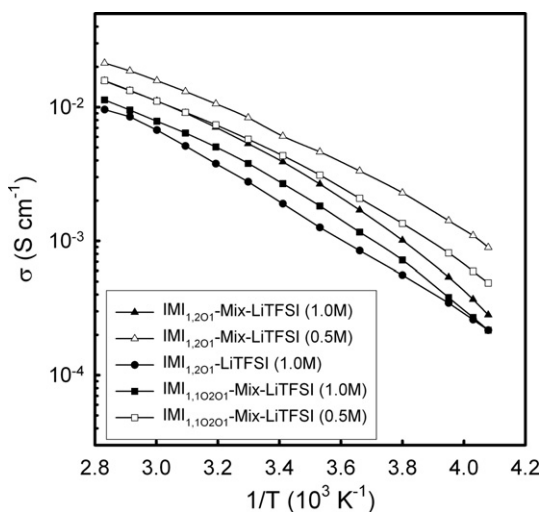


Fig. 3. Ionic conductivity plots as a function of the temperature for the alkoxy IMITFSI-EC/DEC-LiTFSI electrolytes. The conductivity of the IMI_{1,201}TFSI-LiTFSI 1.0 M is also reported as a comparison. The lines are only guides for eyes.

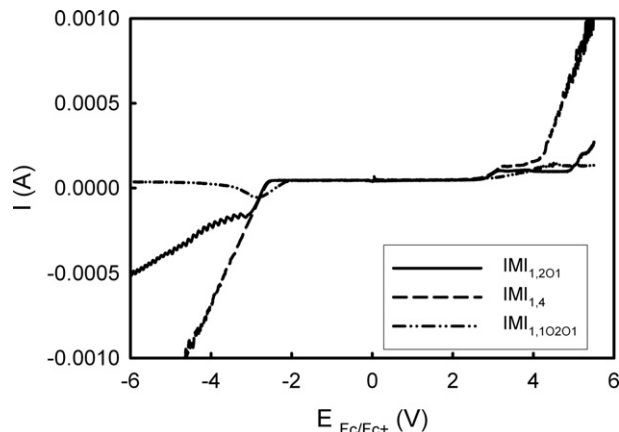


Fig. 4. Sweeps of linear voltammetry of the pure IMIsTFSI ionic liquids vs Fe/Fe³⁺. Scan rate: 10 mV s⁻¹.

electrochemically stable, either from the cathodic or anodic points of view. In particular, the presence of two oxygen units in the ether chain probably favours the cation decomposition, which starts at about 1.0 V. The IMI_{1,201}-based mixtures show ESWs substantially dependent on the Li salt concentration. The more concentrated systems are more stable in terms of anion oxidation (see Table 1).

The investigation of the interfacial stability of IMI-based systems with the Li metal as well as the consequent growth of the passivation film onto the anode are surely necessary to deeply assess the electrochemical stability of such electrolytes. Sweeps of impedance spectroscopy for long storage times are now in progress and will be discussed in a future paper.

3.4. Battery tests

Fig. 6 reports the preliminary tests of the cycling behaviour at room temperature performed by using a LiFePO₄-based electrode for two mixtures, namely IMI_{1,201}TFSI-EC/DEC and IMI_{1,10201}TFSI-EC/DEC, respectively, both doped with LiTFSI in 1.0 M concentration. The charge/discharge rate was varied between 0.1C and 5C. As shown in the figure, the mixtures show good cycling performances at low discharge rate. In the case of IMI_{1,10201}-based systems, specific capacity of 167 mAh g⁻¹, very close to the theoretical one of

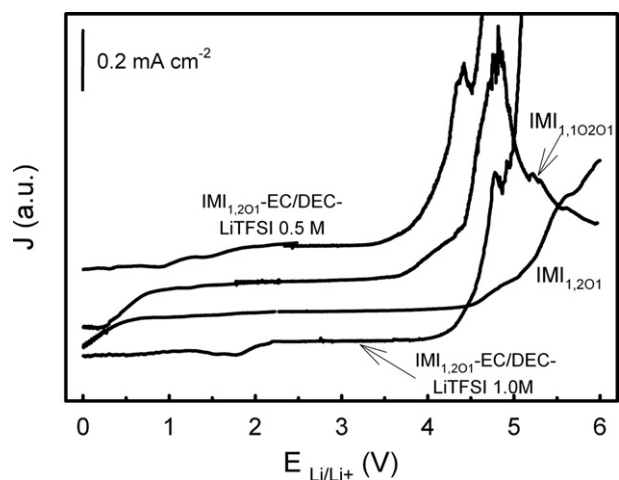


Fig. 5. Sweeps of linear voltammetry of the pure alkoxy IMITFSI and IMI_{1,201}TFSI-EC/DEC-LiTFSI, 0.5 and 1.0 M solutions, respectively. Li was used as the counter and reference electrode and Ni as the working one. Scan rate: 0.2 mV s⁻¹.

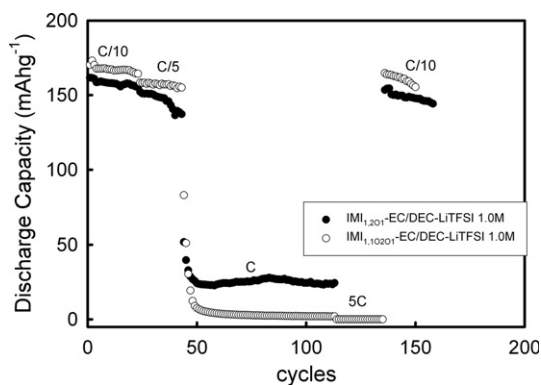


Fig. 6. Room temperature cycling behaviour of Li/LiFePO₄ cells containing the mixtures IMI_{1,201}TFSI-EC/DEC-LiTFSI 1.0 M (open circles) and IMI_{1,10201}TFSI-EC/DEC-LiTFSI 1.0 M (filled circles).

LiFePO₄, are found. A slight decrease up to 157 mAh g⁻¹ is observed at 0.2C. At these C rates, the capacity retention ranges between 98% and 92% at least for 40 cycles and a coulombic efficiency higher than 96% is found. With regards to the IMI_{1,201}-based mixtures, slightly lower values of the discharge capacity are obtained at the same C regime. The discharge capacity of both cells abruptly falls down at higher C rates. However, the cycle performances of the systems are restored by discharging the cell again at low C rate and similar capacity values are found at 0.1C after 150 cycles for both the investigated mixtures. The combination of alkoxy-IMITFSIs with a large amount of EC/DEC mixtures does not seem to be enough to improve the poor rate properties of Li cells including this kind of ionic liquids [19], in contrast to the positive effects recently observed in other electrolytes, as for example, in the case of PYR_{1,4}-PC-LiTFSI [8].

4. Conclusions

In this work, we investigated the functionalization of methyl-imidazolium-based ionic liquids (IMI_{1,R}TFSI) with alkoxy-side chains differing for length and number of oxygen units. Two novel IMIs were then synthesized and characterised in order to evaluate the effect of ether substituents on the physical and electrochemical properties of such ILs. The presence of alkoxy-groups in the cation hinders the crystallization/melting phenomena, at least in presence of TFSI⁻ anions. However, contrary to what found in the case of the pyrrolidinium family (PYRTFSI), small differences are found for what concerns viscosity, ionic conductivity and electrochemical stability by comparing the imidazolium cations (alkoxy- vs alkyl-).

In order to study the eventual beneficial effects of the organic carbonates on the ionic liquids performances, mixtures of IMI_{1,OR}TFSI-EC/DEC-LiTFSI were prepared at different LiTFSI concentrations. Generally speaking, the Li-doped mixtures showed increased conductivity and reduced viscosity. However, the electrochemical stability windows did not exceed 4 V and no improvements in the cycling behaviour of Li cells including the IMIs systems were observed, when the ILs were combined to EC/DEC.

LiFePO₄-based cells with ILs electrolytes displayed capacity retention higher than 92% only at C rate lower than 0.2C. Further works are now in progress to test the combination of such alkoxy-IMIs systems with other additives.

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